

# PATENT ABSTRACTS OF JAPAN

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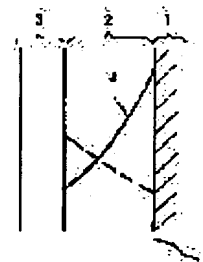
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## (54) FUEL CELL AND ITS APPLIED DEVICE

### (57)Abstract:

**PURPOSE:** To prevent the flooding of water at an oxygen electrode by providing a concentration gradient for at least one or preferably both of a pair of electrodes so that repellency can be high on the electrolyte side while it is low on the electronic conductor side.

**CONSTITUTION:** A cell has a pair of electrodes 2 with electrolyte 1 in between and further has an electronic conductor 3 outside the electrodes 2. The electrode 2 consists of catalytic active components, water repellent components, electrolyte, and a catalytic carrier which has a quality identical to or different from that of the electrolyte 1. An adjustment is carried out so that the concentration of the water repellent body can be higher. Therefore, the conductor 3 side is easy to get wet while an interface 5 to the electrolyte 1 is relatively hard to get wet. Water generated at the interface 5 is moved from a hydrophobic area on the interface 5 side to a hydrophilic area on the conductor 3 side and then removed from the system. At this point, the concentration of water is high on the interface 5 while it is low on the conductor 3 side. The concentration gradient increases the speed at which water is diffused to the conductor 3 side, allows water to be removed very efficiently, and prevents the flooding of water at the interface 5.



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CLAIMS

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[Claim(s)]

[Claim 1] The fuel cell characterized by giving inclination in the hydrogen-oxygen mold fuel cell which has the electrode of a couple on both sides of a polyelectrolyte, and has an electronic conductor on the outside further so that the water repellence by the side of an electronic conductor may become [ the water repellence by the side of an electrolyte ] strong weakly at least at one side of the electrode of said couple.

[Claim 2] The fuel cell characterized by giving a concentration gradient in the hydrogen-oxygen mold fuel cell which has the electrode of a couple on both sides of a polyelectrolyte, and has an electronic conductor on the outside further so that the catalytic activity constituent concentration by the side of an electronic conductor may become [ the catalytic activity constituent concentration by the side of an electrolyte ] high low at least at one side of the electrode of said couple.

[Claim 3] or [ that it is the same as the porosity by the side of an electronic conductor in the hydrogen-oxygen mold fuel cell which has the electrode and electronic conductor of a couple on both sides of a polyelectrolyte in the porosity by the side of one / at least / electrolyte of the electrode of said couple ] -- or the fuel cell characterized by the done thing which it hears.

[Claim 4] or [ that contain an ion conductor homogeneous as an electrolyte, or heterogeneous at least in one side of the electrode of said couple in the hydrogen-oxygen mold fuel cell which has the electrode and electronic conductor of a couple on both sides of a polyelectrolyte, and it is the same as the concentration of the ion conductor by the side of an electronic conductor in the concentration by the side of the electrolyte of this ion conductor ] -- or the fuel cell characterized by making it high.

[Claim 5] The fuel cell characterized by for the ion in claims 1-4 being a proton, and being the ion exchange membrane which an ion conductor becomes from perfluoro sulfonic acid type resin or perfluoro carboxylic acid type resin.

[Claim 6] The fuel cell characterized by the catalytic activity component in claim 2 being platinum.

[Claim 7] The fuel cell characterized by having contained the water-repellent object which becomes at least one side of said electrode from polytetrafluoroethylene and graphites fluoride and such mixture in claim 1, having changed the amount, and giving a concentration gradient.

[Claim 8] The power system characterized by having the fuel cell of claims 1-7 as a source of an output.

[Claim 9] The electric vehicle characterized by having the fuel cell of claims 1-7 as a source of an output.

[Claim 10] The rechargeable battery characterized by having the fuel cell of claims 1-7 as a power source for charge.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the hydrogen-oxygen mold fuel cell which is built over a fuel cell, especially has a polyelectrolyte.

[0002]

[Description of the Prior Art] As an ion conductor, using ion exchange membrane, the general structure of a fuel cell of having a polyelectrolyte installs an oxygen pole and a hydrogen pole in the both sides, and unites with them as indicated in "surface" Vol.26 and No. 1988 [ 12 or ].

[0003] Moreover, two electrodes consist of resin homogeneous as the polytetrafluoroethylene (it is indicated as Following PTFE.) and ion exchange membrane which are the carbon and the binder which are a platinum catalyst and catalyst support as indicated in "DENKIKAGAKU" Vol.53 and No. 1985 [ 10 or ].

[0004] The reaction of a fuel cell mainly consists of the following three kinds.

[0005] (1) Diffusion (2) catalyst surface reaction on the front face of a catalyst of hydrogen and oxygen (a hydrogen pole, oxygen pole)

(3) Proton conduction (inside of the interior of a catalyst, and ion exchange membrane)

The diffusion or the reaction rate in each process influences cell output characteristics greatly. In order to perform efficiently diffusion to the catalyst front face of the hydrogen of (1), and oxygen, using a wave type charge collector is shown in drawing 1 and JP,55-113272,A of drawing 2 of JP,58-204188,A, and JP,60-35472,A, and using the carbon plate which has a rectangle slot is shown in JP,2-260371,A, JP,3-102774,A, and JP,2-86071,A.

[0006] If a wave type charge collector and a carbon plate with a rectangle slot are contacted to an electrode, space will be made in the contact surface and hydrogen or oxygen will be spread in an electrode surface through this space. Although the usually above structures are adopted and a certain amount of output is discovered in the fuel cell which used ion exchange resin, the above-mentioned structure is for supporting the gaseous diffusion from a fuel gas main stream to a catalyst front face to the last.

[0007] However, it is generated also inside the electrode and gaseous diffusion may be able to discover high power further by performing diffusion inside an electrode efficiently. There is the approach of raising the porosity in an electrode as indicated by JP,1-143151,A as an approach for improving this, by this, the contacting efficiency of a catalyst and reactant gas increases and the increment in a reaction rate is enabled.

[0008]

[Problem(s) to be Solved by the Invention] There is the following trouble in the above conventional technique. In order that a reaction may progress by the interface of this exchange film and an oxygen pole at high speed, in an oxygen pole interface, water is generated, the water screen is especially formed with high current density, and the so-called flooding phenomenon produces the proton which has conducted ion exchange membrane. The contacting efficiency of the oxygen gas and the catalyst which have diffused the inside of an electrode for this water screen falls, reduction in output density takes place, and the cell engine performance destabilizes. It is easy to produce especially this phenomenon in the interface of an electrode and ion exchange membrane. If this water screen furthermore exists in an oxygen pole interface, the conduction effectiveness into the oxygen pole of the proton conducted from ion exchange membrane will also fall, and degradation of the cell engine performance will be caused.

[0009] The object of this invention is to offer the hydrogen-oxygen mold fuel cell which has the polyelectrolyte which prevented the flooding of the water in an oxygen pole.

[0010]

[Means for Solving the Problem] In order to attain the object of preventing the flooding of the water in an

oxygen pole, at least on the other hand, this invention is preferably characterized by the thing of the electrode of a couple for which a concentration gradient with the low water repellence by the side of an electronic conductor with the high water repellence by the side of an electrolyte is given at both.

[0011] Moreover, it is characterized by giving a concentration gradient with the high catalytic activity constituent concentration by the side of an electrolyte, and the low catalytic activity constituent concentration by the side of an electronic conductor at least at one side of the electrode of a couple.

[0012] or [ moreover, / that it is the same as the porosity by the side of an electronic conductor in the porosity by the side of one / at least / electrolyte of the electrode of a couple ] -- or it is characterized by enlarging.

[0013] or [ moreover, / that contain an ion conductor homogeneous as an electrolyte, or heterogeneous at least in one side of the electrode of a couple, and it is the same as the concentration of the ion conductor by the side of an electronic conductor in the concentration by the side of the electrolyte of this ion conductor ] - - or it is characterized by making it high.

[0014] according to this invention, the above-mentioned object can be attained -- in addition, the gaseous diffusion in an electrode is further made efficient, and the oxidation reduction reaction produced in the interface of an electrode and ion exchange membrane is accelerated, and the effectiveness that the ion conductivity in an electrode can be improved is acquired.

[0015] The ion conductor in an electrode or concentration distribution of a catalytic activity component, distribution of the magnitude of porosity, or distribution of water-repellent strength may be changing continuously, and may be discontinuous.

[0016] As for an ion conductor, it is desirable that it is the ion exchange membrane which consists of perfluoro sulfonic acid type resin or perfluoro carboxylic acid type resin. A catalytic activity component has desirable platinum.

[0017] It is desirable to contain the water-repellent body which consists of polytetrafluoroethylene and graphites fluoride and such mixture, in order to give inclination to the water-repellent strength in an electrode, and to change the amount.

[0018]

[Function] Since the flooding of water arises in an oxygen pole side, diffusion of oxygen is controlled, and an oxygen-hydrogen mold polyelectrolyte mold fuel cell has the fault that the cell engine performance deteriorates. However, the flooding of water can be prevented by making the water repellence of an electrode small by the electronic conductor side highly by the electrolyte side. Since the water repellence of the interface of an ion conductor and an electrode is strong, even if water invades, the water screen is because it does not become, but it becomes a drop and the coat to a catalytic activity component is prevented.

[0019] The dotted line showed the hydrophilic level in an electrode to drawing 1 . In an electronic conductor 3 side, it is easy to get wet in water relatively, and hard to get wet in water relatively in the interface 5 with an ion conductor (electrolyte) 1. Therefore, the water generated by the interface 5 moves to the hydrophilic field by the side of an electronic conductor 3 from the hydrophobic field by the side of an interface 5, and is removed by evaporation etc. out of a system. In this case, the concentration of water becomes it is high and low by the interface 5 at an electronic conductor 3 side. The diffusion rate of the water by the side of an electronic conductor 3 becomes large according to this concentration gradient, it becomes possible to be efficient and to remove water, and the flooding of the water in an interface 5 can be prevented still more efficiently.

[0020] Although the electrode of drawing 2 is prepared so that a catalyst component may become high concentration by the electrolyte 21 side, by this, electrode reaction becomes easy to advance by the interface 26 by the side of an electrolyte 21, and the cell engine performance improves. This is based on the following reasons. That is, the proton conducted from the electrolyte 21 is emitted to the exterior of an electrolyte 21 by the interface 26, and serves as water in response to oxygen and an electron. Or this proton is conducted to the electrolyte contained in an electrode 22, and follows the same process. Therefore, proton concentration falls, so that it goes to an electronic conductor 23 side by the interface 26 most highly. Since a reaction rate is proportional to proton concentration, it will be the highest at an interface 26.

[0021] Since electrode reaction is produced on a catalyst, as for a reaction rate, the direction with many amounts of catalysts as a reaction site becomes large. In the electrode which has distribution of a catalyst component like drawing 2 by such reason, according to an interface 26, the reaction rate of the reduction reaction of oxygen can be more remarkably [ than the conventional thing ] high, and the cell engine performance can be raised. Moreover, although water-repellent object concentration is high by the interface

26 like drawing 2 , since the water-repellent body has the effectiveness which covers a catalyst component, a reaction rate will be reduced. The electrode of drawing 2 has sufficient catalyst front face to advance a reaction, even if catalyst surface area is large and is somewhat covered with the water-repellent body, since catalyst constituent concentration is high by the interface 26.

[0022] In the electrode of drawing 3 , the porosity in an electrode has a curve 36 or distribution of 37. An important thing needs to be distribution to which porosity does not fall by the electrolyte 31 side. As for each electrode shown in drawing 3 from drawing 1 , the concentration of the water-repellent body is high by electrolytes 1 and 21 and 31 side. Although the water-repellent body is effective in hydrophobing of an electrode, when concentration becomes high, it covers, the front face, i.e., the reaction site, of a catalyst component, and there is a fault of controlling progress of catalytic reaction.

[0023] A policy may be carried out for preventing this and catalyst surface area may be increased for a catalyst component as high concentration like drawing 2 . Moreover, there is the approach of lessening coat area on the front face of a catalyst with a water-repellent object by making porosity high, as shown in drawing 3 . This is shown in drawing 6 . Drawing 6 (1) shows the structure near [ in an electrode when porosity is small ] the catalyst. The catalyst 61 is supported by catalyst support 62, and since water-repellent object concentration is high, the catalyst is covered in drawing 6 (1) by the water-repellent object 63.

Although the catalyst 64 enclosed with the dotted line located inside the support 62 shown by drawing 6 (1) is not directly covered by the water-repellent body, diffusion of the gas which lets pore 65 pass cannot take place easily, and the inside catalyst 64 is inactive with the structure of drawing 6 (1) as a result. On the other hand, drawing 6 (2) is the structure at the time of making the porosity of the electrode of drawing 6 (1) high. Since pore 69 existed newly, the inside catalyst 70 shown by the dotted line was exposed to the pore side. Therefore, gas 68 contacts a catalyst 70 easily and an active site is used effectively. Thus, a catalyst can be used effectively by the increment in porosity and it is effective in gaseous diffusion being promoted further and the contacting efficiency of a catalyst front face and gas improving. Since catalytic reaction tends to advance by the interface 38 of an electrode 32 and an electrolyte 31 like especially drawing 3 , if it pulls with improvement in a reaction rate when the porosity in this interface field is high, improvement in the cell engine performance can be aimed at.

[0024] As for the electrode of drawing 4 , the electrolyte in an electrode has distribution of curves 48 and 49. Importance here is considering as distribution to which an electrolyte's does not fall by the interface 50 side. The proton emitted from an electrolyte 41 is conducted to the electrolyte distributed in the electrode, the oxygen in a gaseous phase is contacted through this distributed electrolyte, and a reaction advances. Since the surface area of the electrolyte distributed in the electrode is large and the touch area of a proton and oxygen also becomes large, distributing an electrolyte in an electrode promotes progress of a reaction. However, in an electrode to which the electrolytic concentration in an electrode falls by the interface 50 in drawing 4 , since the surface area of the electrolyte distributed in the electrode decreases by the interface 50 with the most prosperous reaction, the touch area of oxygen and a proton becomes small, and progress of a reaction is controlled. Therefore, distribution to which the electrolyte distributed in the electrode as mentioned above does not fall by the interface 50 side is required.

[0025] An electrode 56 is divided into three layers and the electrode of drawing 5 is the example from which concentration distribution of a water-repellent object changed at the step. As for the electrode of drawing 5 , the concentration of the water-repellent body has become high at an electrolyte 51 side. Since the flooding of water arose in an oxygen pole side as mentioned above in the case of an oxygen-hydrogen mold polyelectrolyte mold fuel cell, diffusion of oxygen was controlled, and there was a fault that the cell engine performance deteriorated. However, since water-repellent object concentration is high according to the interface 57 of an electrolyte 51 and a catalyst 56 in the electrode of drawing 5 , the flooding of water is prevented. Since water-repellent object concentration is high, even if hydrophobicity is high and water invades at an interface 57 for this reason, the water screen is because it does not become, but it becomes a drop and the coat of a catalyst component is prevented. The level of a hydrophilic property tends to get wet in water relatively in an electronic conductor 55 side, and cannot get wet easily in water relatively in an interface 57. Therefore, the water generated by the interface 57 moves to the hydrophilic field by the side of an electronic conductor 55 from the hydrophobic field by the side of an interface 57, and is removed by evaporation etc. out of a system. In this case, the concentration of water becomes it is high and low by the interface 57 at an electronic conductor 55 side. The diffusion rate of the water by the side of an electronic conductor 55 becomes large according to this concentration gradient, it becomes possible to be efficient and to remove water, and the flooding of the water in an interface 57 can be prevented still more efficiently.

[0026]

[Example] The fundamental cell structure of this invention is shown in drawing 1. A cell has the electrode 2 of a couple on both sides of an electrolyte 1, and has an electronic conductor 3 on the outside further.

Drawing 1 shows only the electrode and electronic conductor with which one [ of an electrolyte 1 ] one [ a part and ] was equipped. It consists of electrolytes, catalyst support, etc. homogeneous [ an electrode 2 ] as a catalytic activity component, a water-repellent body constituent, and an electrolyte 1, or heterogeneous. The concentration distribution 4 of a water-repellent object was shown in drawing 1. It is prepared so that the water-repellent object concentration by the side of ion exchange membrane (electrolyte) 1 may become high.

[0027] The cell of drawing 2 consists of an electrolyte 21, an electrode 22, and an electronic conductor 23. It consists of electrolytes, catalyst support, etc. homogeneous [ an electrode 22 ] as a catalyst component, a water-repellent body constituent, and an electrolyte 21, or heterogeneous. Concentration distribution of the water-repellent body 24 and the catalytic activity component 25 was shown in drawing 2. By the electrolyte 21 side, both are prepared for concentration so that it may become high. The electrode of drawing 3 R> 3 consists of an electrolyte 31, an electrode 32, and an electronic conductor 33. It consists of electrolytes, catalyst support, etc. homogeneous [ an electrode 32 ] as a catalytic activity component, a water-repellent body constituent, and an electrolyte 31, or heterogeneous. Concentration distribution and the porosity distribution 36 and 37 of the water-repellent body 34 and the catalytic activity component 35 were shown in drawing 3. It has prepared so that all may become high by the electrolyte 31 side. Although it is necessary to choose either about the porosity distribution 36 and 37, an important thing is not making it porosity not become low by the electrolyte 31 side.

[0028] The cell of drawing 4 consists of an electrolyte 41, an electrode 42, and an electronic conductor 43. It consists of electrolytes, catalyst support, etc. homogeneous [ an electrode 42 ] as a catalytic activity component, a water-repellent body constituent, and an electrolyte 41, or heterogeneous. Distribution was shown in drawing 4 about the water-repellent body 44, the catalytic activity component 45, electrolytes 48 and 49, and porosity 46 and 47. Electrolytes 48 and 49 are homogeneous as an electrolyte 41, or heterogeneous, and need to choose one from distribution of 48 or 49. An important thing is not giving distribution to which the electrolyte constituent concentration in an electrode falls by the electrolyte 41 side.

[0029] Electrode structure when concentration distribution is discontinuous is shown in drawing 5. A cell consists of an electrolyte 51, electrodes 52, 53, and 54, and an electronic conductor 55. The electrode is divided into three layers 52, 53, and 54, and concentration distribution of the water-repellent body included in each, a catalytic activity component, and an electrolyte changes gradually like drawing 5. Moreover, the porosity in an electrode can also be gradually changed like drawing 5. In drawing 5, although only concentration distribution of one kind of thing is indicated, the water-repellent body, a catalytic activity component, an electrolyte, and each of porosity may be changed gradually. Moreover, at drawing 5, especially although a catalyst consists of three layers, there is no definition in the number of layers. Moreover, with the electronic conductor described above, so-called good charge collector, so-called good diffusion layer, etc. of electronic conduction nature are included.

[0030] Next, the preparation approach of an electrode of having concentration distribution as shown in drawing 1 - drawing 5 is indicated. The approach of forming continuous concentration distribution like drawing 1 - drawing 4 first is indicated. The applying method is suitable for adjustment of distribution of a water-repellent object. This is the method of pasting up this electrode and an ion conductor, after applying the liquid which made the catalyst front face beforehand formed as a thin film on the electronic conductor distribute the water-repellent body by brushing etc. For example, distribution of drawing 1 of 4 is producible by applying the diluent which distributed PTFE in water to the catalyst bed front face applied on an electronic conductor like carbon paper.

[0031] The applying method is suitable also for adjustment of distribution of an ion conductor. This is the way of applying the liquid which made the catalyst front face beforehand formed as a thin film on the electronic conductor distribute an ion conductor by brushing etc. For example, 48 of drawing 4 and distribution of 49 are producible by applying the liquid distributed by isopropanol alcohol etc. with ion exchange resin, such as Nafion 117, to the catalyst bed front face applied on an electronic conductor like carbon paper.

[0032] The approach of forming the catalyst bed which supported noble metals beforehand for adjustment of a catalyst component as a thin film on an electronic conductor, and newly adding a noble-metals component from the front face is good. There is the approach of making it deposit from gaseous phases, such as vacuum evaporatio and ion implantation, as the approach etc.

[0033] It is possible by contacting a steam on the catalyst front face beforehand formed in preparation of

porosity as a thin film, for example on the electronic conductor. Since pore is formed into a catalyst when a steam invades into a catalyst bed, adjustment of various magnitude and the pore of distribution is possible by the flow rate of a steam, or preparation of concentration carrier gas.

[0034] Next, the preparation of the concentration distribution shown by drawing 5 is indicated. Various concentration of a catalyst, support, a water-repellent object, and an ion conductor is prepared, and the catalyst beds 52-54 in drawing 5 are prepared beforehand, and are slurred. Next, a catalyst bed 54 is first applied to an electronic conductor 55. Furthermore, after carrying out sequential spreading of the catalyst beds 53 and 52, the structure of drawing 5 can be formed by pasting up an ion conductor 51. Concentration of a catalyst, the water-repellent body, and an ion conductor can be made the shape of a step like drawing 5 by the above approach. On the other hand, adjustment of porosity distribution is carried out like the next, and is performed. It is the approach of changing the amount of the water made containing in case a catalyst bed 52-54 is prepared the first, respectively, or an organic solvent. Thus, if the catalyst bed prepared and applied is dried, in case water or an organic solvent evaporates, pore is formed, and the magnitude and distribution can be freely controlled with the amount of the water added to the catalyst bed, and an organic solvent, a rate of drying, etc. Moreover, porosity can be changed by contacting a steam on the front face of the catalyst bed 54 applied to the electronic conductor 55 as the 2nd approach. The catalyst bed 53 of the 2nd layer is further applied on a catalyst bed 54 after desiccation, and same actuation is performed. It is possible to change distribution of the porosity in a catalyst bed also by such approach.

[0035] Next, the application system of the above-mentioned fuel cell is explained. Drawing 10 shows a power system. After controlling hydrogen gas 102 and oxygen gas 101 by the regulator 103, it supplies and generates electricity to a fuel cell 104. After the output from a fuel cell 104 is changed into an alternating current by the inverter 105, it is supplied to the power systems 106, such as a motor, and operates the actuation system 107. Hydrogen gas 102 can also use what was generated with refining vessels, such as a methanol.

[0036] Drawing 11 shows another power system. After controlling hydrogen gas 112 and oxygen gas 111 by the regulator 113, it supplies and generates electricity to a fuel cell 114. After the output from a fuel cell 114 is changed into an alternating current by the inverter 115, it is supplied to the power systems 116, such as a motor, and operates the actuation system 117. Hydrogen gas 112 can also use what was generated with refining vessels, such as a methanol. It is possible for the output from a fuel cell to be able to charge a rechargeable battery 118, and to, supply the output of this rechargeable battery 118 to a power system through an inverter 119 on the other hand.

[0037] It is possible to supply the output from either or both of a fuel cell 114 and the rechargeable batteries 118 to a power system in this system.

[0038] Moreover, the system of drawing 10 and drawing 11 may be carried in an electric vehicle.

[0039] (Example 1 of an experiment) The structure of the electrode used for drawing 7 in this example of an experiment is shown. The inside B of drawing consists of an electrolyte membrane 71, the hydrogen pole 74, an oxygen pole 73, and a diffusion layer 75. Du Pont Nafion 117 was used as an electrolyte membrane. Moreover, about 100 micrometers of pore size and carbon paper with a thickness of 100 micrometers were used for the diffusion layer. The presentation of electrodes 73 and 74 was shown in a table 1.

[0040]

[A table 1]

表 1

電 極 項 目	7 3	7 2	7 4
P T F E	0 . 4 6	0 . 8 5	1 . 5
ナフイオン 1 1 7	0 . 5 1	0 . 5 1	1 . 0
白 金	3 . 2 2	3 . 2 2	3 . 0
ε	4 0	4 0	4 0

単位 mg/cm<sup>2</sup> (εのみvol%)

[0041] The inside A of drawing is constituted by the oxygen pole which consists of an electrolyte membrane 71, a hydrogen pole 74, and 72 and 73. The presentation of the oxygen poles 72 and 73 and the hydrogen pole 74 is shown in a table 1. The description of Electrode A is that the oxygen pole serves as a bilayer and the concentration of PTFE which is the water-repellent body in the electrode layer 72 by the side of an electrolyte membrane 71 is higher than the outside electrode layer 73.

[0042] The method of producing an electrode is shown below. Carbon paper 150cm<sup>2</sup> of the above-mentioned first The electrode slurry prepared upwards according to the presentation of a table 1 was applied to homogeneity. Carbon paper was cut down after this and the 30mmx30mm electrode was created.

[0043] Production of the oxygen electrodes 72 and 73 in [ A ] drawing 7 was performed as follows. That is, after applying the electrode of 73 first on carbon paper as mentioned above, the electrode layer of further 72 was applied.

[0044] Adhesion to Nafion of the electrode prepared by the above approach was performed by hot pressing. It is the thing of the structure of A and B 100kg/cm<sup>2</sup> It pressed at the temperature of 120 degrees C with the pressure for 15 minutes. The result of having examined a nest and the current-voltage characteristic for the electrodes A and B produced as mentioned above in the cel was shown in drawing 8 . the electrode B by the conventional example -- limiting current density -- 200 mA/cm<sup>2</sup> it is -- a thing -- receiving -- the limiting current density of the electrode A of this invention -- 300 mA/cm<sup>2</sup> It exceeded. Thus, the cell engine performance was able to be substantially improved by bilayer-izing an oxygen pole and making high water-repellent body concentration of the electrode by the side of an electrolyte membrane.

[0045] (Example 2 of an experiment) The cell used for drawing 9 in this example of an experiment is shown. A cell consists of the Nafion film 91, a hydrogen electrode 74, oxygen electrodes 92 and 73, and a diffusion layer 93. The presentation of electrodes 92, 73, and 74 is shown in a table 2.

[0046]

[A table 2]



表 2

電 極 項 目	7 3	9 2	7 4
P T F E	0 . 4 6	0 . 8 5	1 . 5
ナフイオン 1 1 7	0 . 5 1	0 . 5 1	1 . 0
白 金	3 . 2 2	3 . 2 2	3 . 0
$\epsilon$	4 0	5 0	4 0

単位  $\text{mg}/\text{cm}^2$  ( $\epsilon$  のみ vol%)

[0047] As for the description of this electrode, the oxygen pole is bilayer-ized, and to the porosity of the electrode 73 by the side of a diffusion layer being 40%, the electrode 92 by the side of the Nafion film is prepared so that porosity may become 50%.

[0048] Adjustment of porosity was performed as follows. After the electrode 73 mixed 50-% of the weight (wt%) platinum support carbon 3.86g, 0.27g of PTFE60% dispersion liquid, 0.31g of isopropyl alcohol 5% solutions of Nafion, and four cc of pure water with the stone milling machine, it was applied to previous carbon paper. This is the electrode 73 of drawing 9. This was dried 5h at 80 degrees C. Next, after mixing 50wt% platinum support carbon 3.86g, 0.27g of PTFE60% dispersion liquid, 0.31g of isopropyl alcohol 5% solutions of Nafion, and eight cc of pure water with a stone milling machine to this electrode at a pan, the catalyst was finished to the electrode of the point applied further. This is the electrode 92 of drawing 9. Since the electrode 92 contained pure water in the preparation phase so much more than an electrode 73, at the time of desiccation, this water evaporated, pore was formed and porosity became high as a result.

[0049] The voltage-current property of Electrode C was shown in drawing 8. To the electrode A which consists of an electrode of 40% of porosity, limiting current density exceeded 400 mA/cm<sup>2</sup>, and the cell engine performance of Electrode [ 50% and ] C improved the porosity of an oxygen pole further.

[0050]

[Effect of the Invention] The activity of the oxygen electrode of the oxygen-hydrogen mold fuel cell which has a polyelectrolyte by this invention can be improved more nearly substantially than the conventional thing, and the cell engine performance can be improved.

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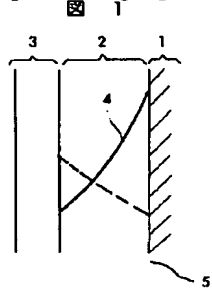
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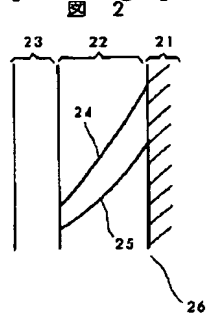
DRAWINGS

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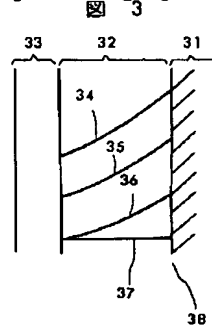
[Drawing 1]



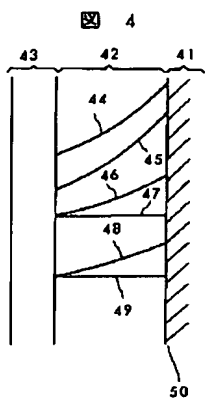
[Drawing 2]



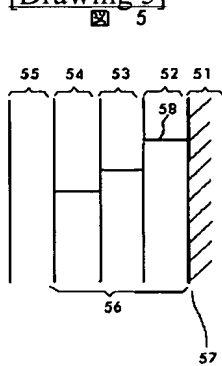
[Drawing 3]



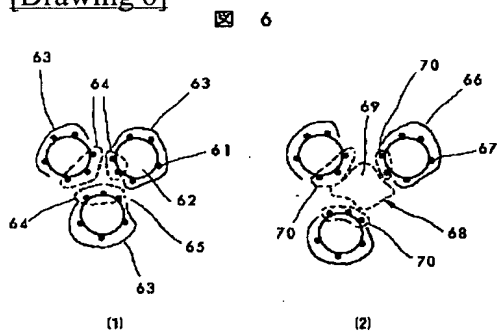
[Drawing 4]



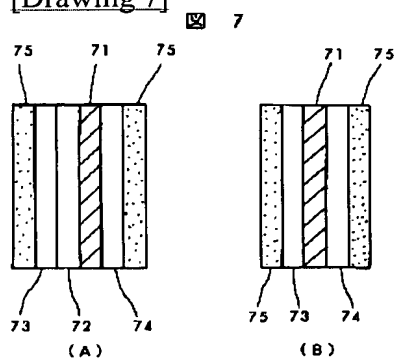
[Drawing 5]



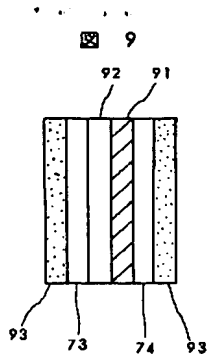
[Drawing 6]



[Drawing 7]

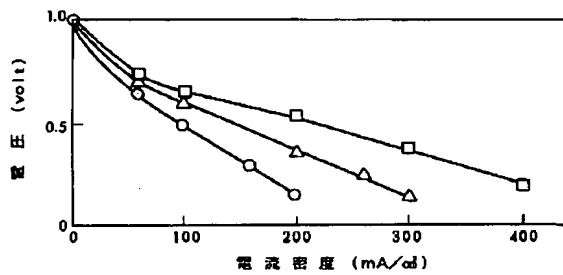


[Drawing 9]



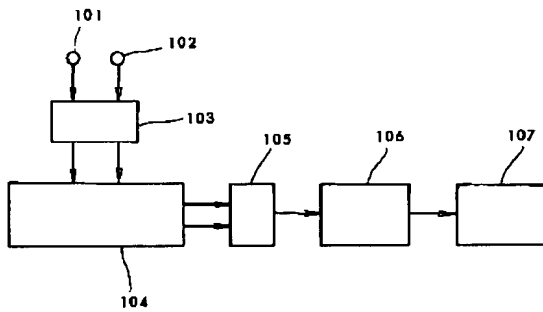
[Drawing 8]

図 8



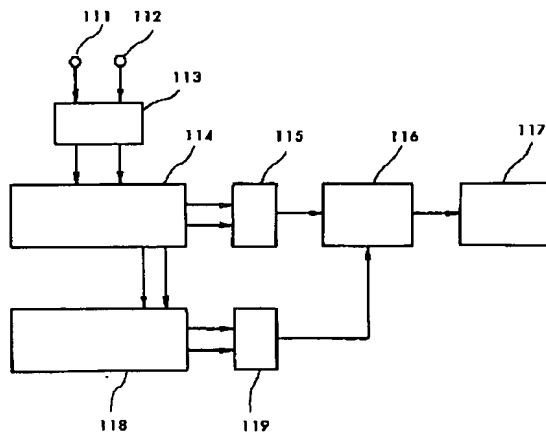
[Drawing 10]

図 10



[Drawing 11]

図 11



[Translation done.]

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : HITACHI LTD

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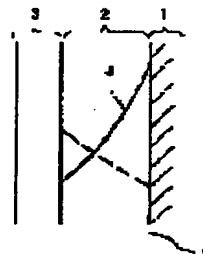
(72)Inventor : MURANAKA TADASHI  
IMAHASHI JINICHI  
HORIBA TATSUO  
NISHIMURA SHIGEOKI

## (54) FUEL CELL AND ITS APPLIED DEVICE

## (57)Abstract:

**PURPOSE:** To prevent the flooding of water at an oxygen electrode by providing a concentration gradient for at least one or preferably both of a pair of electrodes so that repellency can be high on the electrolyte side while it is low on the electronic conductor side.

**CONSTITUTION:** A cell has a pair of electrodes 2 with electrolyte 1 in between and further has an electronic conductor 3 outside the electrodes 2. The electrode 2 consists of catalytic active components, water repellent components, electrolyte, and a catalytic carrier which has a quality identical to or different from that of the electrolyte 1. An adjustment is carried out so that the concentration of the water repellent body can be higher. Therefore, the conductor 3 side is easy to get wet while an interface 5 to the electrolyte 1 is relatively hard to get wet. Water generated at the interface 5 is moved from a hydrophobic area on the interface 5 side to a hydrophilic area on the conductor 3 side and then removed from the system. At this point, the concentration of water is high on the interface 5 while it is low on the conductor 3 side. The concentration gradient increases the speed at which water is diffused to the conductor 3 side, allows water to be removed very efficiently, and prevents the flooding of water at the interface 5.



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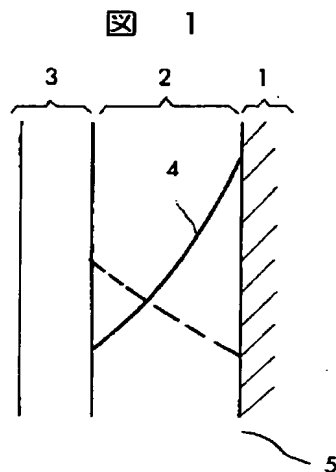
(54)【発明の名称】 燃料電池及びその応用装置

(57)【要約】

【目的】高分子電解質を有する水素-酸素型燃料電池において、酸素極とイオン伝導体(電解質)との界面での水のフラッディングを防止する。

【構成】電子伝導体1と電解質2との間に位置する燃料電池用電極の撥水性を電解質2側で強く、電子伝導体1側で弱くして濃度分布をもたせた。

【効果】従来の電極に対して2~3倍の出力密度を得ることができる。



## 【特許請求の範囲】

【請求項1】高分子電解質を挟んで一对の電極を有し更にその外側に電子伝導体を有する水素-酸素型燃料電池において、前記一对の電極の少なくとも一方に電解質側の撥水性が強く電子伝導体側の撥水性が弱くなるように勾配をもたせたことを特徴とする燃料電池。

【請求項2】高分子電解質を挟んで一对の電極を有し更にその外側に電子伝導体を有する水素-酸素型燃料電池において、前記一对の電極の少なくとも一方に電解質側の触媒活性成分濃度が高く電子伝導体側の触媒活性成分濃度が低くなるように濃度勾配をもたせたことを特徴とする燃料電池。

【請求項3】高分子電解質を挟んで一对の電極及び電子伝導体を有する水素-酸素型燃料電池において、前記一对の電極の少なくとも一方の電解質側の気孔率を電子伝導体側の気孔率と同じか或いはきくしたことを特徴とする燃料電池。

【請求項4】高分子電解質を挟んで一对の電極及び電子伝導体を有する水素-酸素型燃料電池において、前記一对の電極の少なくとも一方に電解質と同質あるいは異質のイオン伝導体を含有し、該イオン伝導体の電解質側の濃度を電子伝導体側のイオン伝導体の濃度と同じか或いは高くしたことを特徴とする燃料電池。

【請求項5】請求項1～4におけるイオンがプロトンであり、イオン伝導体がパーフルオロスルホン酸樹脂あるいはパーフルオロカルボン酸樹脂からなるイオン交換膜であることを特徴とする燃料電池。

【請求項6】請求項2における触媒活性成分が白金であることを特徴とする燃料電池。

【請求項7】請求項1において、前記電極の少なくとも一方にポリテトラフルオロエチレン、フッ化黒鉛あるいはこれらの混合物からなる撥水体を含有し、その量を変化させて濃度勾配をもたせたことを特徴とする燃料電池。

【請求項8】請求項1～7の燃料電池を出力源として有することを特徴とする動力システム。

【請求項9】請求項1～7の燃料電池を出力源として有することを特徴とする電気自動車。

【請求項10】請求項1～7の燃料電池を充電用電源として備えたことを特徴とする二次電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は燃料電池に係り、特に高分子電解質を有する水素-酸素型燃料電池に関する。

## 【0002】

【従来の技術】高分子電解質を有する燃料電池の一般的構造は「表面」Vol. 26, No. 12, 1988年に開示されているように、イオン伝導体としてイオン交換膜を使用しその両側に酸素極、水素極を設置して一体化したものである。

【0003】また、「DENKIKAGAKU」Vol. 53, No. 10, 1985年に開示されているように、両電極は白金触媒、触媒担体であるカーボン、結着剤であるポリテトラフルオロエチレン（以下PTFEと記載する。）及びイオン交換膜と同質の樹脂からなる。

【0004】燃料電池の反応は主に次の三種類からなる。

【0005】（1）水素及び酸素の触媒表面への拡散

（2）触媒表面反応（水素極、酸素極）

（3）プロトン伝導（触媒内部、イオン交換膜内）

それぞれのプロセスでの拡散あるいは反応速度が電池出力特性に大きく影響する。（1）の水素及び酸素の触媒表面への拡散を効率的に行うために、波型集電体を使用することが特開昭58-204188号公報の図2、特開昭60-35472号公報の図1及び特開昭55-113272号公報に示されており、矩形溝を有するカーボンプレートを使用することが特開平2-260371号公報、特開平3-102774号公報及び特開平2-86071号公報に示されている。

【0006】波型集電体や矩形溝付きカーボンプレートを電極に接触させると接触面に空間ができ、この空間を通して水素あるいは酸素が電極表面に拡散する。イオン交換樹脂を使用した燃料電池では通常上記のような構造が採用されており、ある程度の出力が発現されているが、上記の構造はあくまでも燃料ガス本流から触媒表面までのガス拡散を支援するためのものである。

【0007】しかし、ガス拡散は電極内部でも生じており、電極内部での拡散を効率的に行うことにより更に高出力を発現できる可能性がある。これを改善するための方法として特開平1-143151号公報に開示されているように電極内の気孔率を高める方法があり、これによって触媒と反応ガスとの接触効率が高まり反応速度の増加が可能であるとしている。

## 【0008】

【発明が解決しようとする課題】以上の従来技術には次の問題点がある。イオン交換膜を伝導してきたプロトンは、該交換膜と酸素極との界面で反応が高速に進むため酸素極界面では水が生成され、特に高電流密度では水膜が形成され、いわゆるフラッディング現象が生じる。この水膜のために電極内を拡散してきた酸素ガスと触媒との接触効率が低下し、出力密度の減少が起こり電池性能が不安定化する。この現象は特に電極とイオン交換膜との界面で生じやすい。さらに該水膜が酸素極界面に存在すると、イオン交換膜から伝導してきたプロトンの酸素極内への伝導効率も低下して電池性能の劣化を引き起こす。

【0009】本発明の目的は、酸素極における水のフラッディングを防止した高分子電解質を有する水素-酸素型燃料電池を提供することにある。

## 【0010】



【課題を解決するための手段】酸素極における水のフラッディングを防止するという目的を達成するために、本発明は一对の電極の少なくとも一方好ましくは両方に電解質側の撥水性が高く電子伝導体側の撥水性が低い濃度勾配をもたせることを特徴とする。

【0011】また、一对の電極の少なくとも一方に電解質側の触媒活性成分濃度が高く電子伝導体側の触媒活性成分濃度が低い濃度勾配をもたせることを特徴とする。

【0012】また、一对の電極の少なくとも一方の電解質側の気孔率を電子伝導体側の気孔率と同じか或いは大きくすることを特徴とする。

【0013】また、一对の電極の少なくとも一方に電解質と同質あるいは異質のイオン伝導体を含有し、該イオン伝導体の電解質側の濃度を電子伝導体側のイオン伝導体の濃度と同じか或いは高くすることを特徴とする。

【0014】本発明によれば、上記目的を達成できることに加えて、更に電極内のガス拡散を高効率化し、電極とイオン交換膜の界面で生じる酸化還元反応を加速し、また電極内のイオン導電性を向上することができるという効果が得られる。

【0015】電極内のイオン伝導体或いは触媒活性成分の濃度分布、気孔率の大きさの分布、或いは撥水性の強さの分布は、連続的に変化していてもよいし、不連続であってもよい。

【0016】イオン伝導体は、パーフルオロスルホン酸樹脂あるいはパーフルオロカルボン酸樹脂からなるイオン交換膜であることが望ましい。触媒活性成分は白金が望ましい。

【0017】電極内の撥水性の強さに勾配をもたせるためにポリテトラフルオロエチレン、フッ化黒鉛あるいはこれらの混合物からなる撥水体を含有し、その量を変化させることが望ましい。

【0018】

【作用】酸素-水素型高分子電解質型燃料電池は、酸素極側で水のフラッディングが生じるために酸素の拡散が抑制され、電池性能が劣化するという欠点がある。しかし、電極の撥水性を電解質側で高く電子伝導体側で小さくすることにより、水のフラッディングを防止することができる。なぜならばイオン伝導体と電極との界面の撥水性が強いので水が侵入してきても水膜とはならず液滴となり触媒活性成分への被覆が防止されるからである。

【0019】図1に電極内の親水性レベルを点線で示した。電子伝導体3側では相対的に水に濡れやすく、イオン伝導体(電解質)1との界面5では相対的に水に濡れにくい。従って界面5で生成された水は、界面5側の疎水性領域から電子伝導体3側の親水性領域へ移動し蒸発等により系外に除去される。この際に水の濃度は界面5で高く電子伝導体3側で低くなる。この濃度勾配により電子伝導体3側への水の拡散速度が大きくなり、水を高効率で除去することが可能となり、界面5における水の

フラッディングを更に効率良く防止することが出来る。

【0020】図2の電極は触媒成分が電解質21側で高濃度になるように調製されているが、これによって電解質21側の界面26で電極反応が進行し易くなり電池性能が向上する。これは次のような理由によるものである。即ち電解質21から伝導してきたプロトンは界面26で電解質21の外部に放出され、酸素と電子をうけて水となる。或いは該プロトンは電極22内に含有する電解質に伝導し同様の過程を辿る。従ってプロトン濃度は界面26で最も高く電子伝導体23側に行くほど低下する。反応速度はプロトン濃度に比例するので界面26で最も高いことになる。

【0021】電極反応は触媒上で生じるので反応サイトとしての触媒量が多い方が反応速度は大きくなる。このような理由で図2の様な触媒成分の分布をもつ電極では界面26で、酸素の還元反応の反応速度が従来のものよりも著しく高く、電池性能を向上させることができる。また図2のように撥水体濃度が界面26で高くなっているが、撥水体は触媒成分を被覆する効果があるので反応速度を低下させてしまう。図2の電極は触媒成分濃度が界面26で高くなっているため触媒表面積が大きく、撥水体により多少被覆されても反応を進行させるに十分な触媒表面を有している。

【0022】図3の電極では電極内の気孔率が曲線36或いは37の分布を有するものである。重要なことは気孔率が電解質31側で低下しない分布である必要がある。図1から図3に示された電極はいずれも電解質1、21、31側で撥水体の濃度が高くなっている。撥水体は電極の疎水化に有効であるが、濃度が高くなった場合には触媒成分の表面即ち反応サイトを被覆してしまい、触媒反応の進行を抑制するという欠点がある。

【0023】これを防止するための方策として触媒成分を図2のように高濃度として触媒表面積を増加させることがある。また、図3に示したように気孔率を高くすることにより、撥水体による触媒表面の被覆面積を少なくする方法がある。これを図6に示す。図6(1)は気孔率が小さい場合の電極内の触媒近傍の構造を示したものである。図6(1)では触媒61が触媒担体62に担持されており、撥水体濃度が高いので撥水体63により触媒が被覆されている。図6(1)で示した担体62の内側に位置する点線で囲った触媒64は直接、撥水体に被覆されていないが、細孔65を通してのガスの拡散は起こりにくく、結果的に図6(1)の構造では内側の触媒64は不活性である。これに対して図6(2)は図6

(1)の電極の気孔率を高くした場合の構造である。気孔69が新しく存在するので点線で示した内側の触媒70が気孔側に露出したようになっている。従ってガス68が容易に触媒70に接触し活性サイトが有効利用される。このように気孔率の増加により触媒を有効利用でき、さらにガス拡散が促進され触媒表面とガスとの接触

効率が向上される効果がある。特に図3のように電極32と電解質31との界面38では触媒反応が最も進行しやすいので、該界面領域での気孔率が高い場合には反応速度の向上とひいては電池性能の向上を図ることが出来る。

【0024】図4の電極は電極内の電解質が曲線48、49の分布を有するものである。ここでの重要性は、電解質が界面50側で低下しないような分布とすることである。電解質41から放出されるプロトンは電極内に分散された電解質に伝導し、この分散された電解質を通して気相中の酸素と接触して反応が進行する。電極内に分散された電解質の表面積は大きいとプロトンと酸素との接触面積も大きくなるので、電極内に電解質を分散させることは反応の進行を促進するものである。しかし、電極内の電解質濃度が図4内の界面50で低下するような電極では電極内に分散された電解質の表面積が、反応が最も盛んな界面50で減少するので酸素とプロトンとの接触面積が小さくなり、反応の進行が抑制される。従って前述のように電極内に分散された電解質が界面50側で低下しないような分布が必要である。

【0025】図5の電極は電極56が3層に分離されたものであり、撥水体の濃度分布がステップで変化した例である。図5の電極は撥水体の濃度が電解質51側で高くなっている。酸素-水素型高分子電解質型燃料電池の場合には前述のように酸素極側で水のフラッディングが生じるために酸素の拡散が抑制され、電池性能が劣化するという欠点があった。しかし図5の電極では電解質51と触媒56との界面57で撥水体濃度が高くなっているため、水のフラッディングが防止される。なぜならば界面57では撥水体濃度が高いので疎水性が高くなっており、このため水が侵入してきても水膜とはならず液滴となり触媒成分の被覆が防止されるからである。親水性のレベルは電子伝導体55側では相対的に水に濡れやすく、界面57では相対的に水に濡れにくい。従って界面57で生成された水は、界面57側の疎水性領域から電子伝導体55側の親水性領域へ移動し蒸発等により系外に除去される。この際に水の濃度は界面57で高く電子伝導体55側で低くなる。この濃度勾配により電子伝導体55側への水の拡散速度が大きくなり、水を高効率で除去することが可能となり、界面57における水のフラッディングを更に効率良く防止することが出来る。

【0026】

【実施例】本発明の基本的な電池構造を図1に示す。電池は電解質1を挟んで一対の電極2を有し更にその外側に電子伝導体3を有する。図1は電解質1の一部とその一方の側に備えられた電極及び電子伝導体のみを示している。電極2は触媒活性成分、撥水体成分、電解質1と同質あるいは異質の電解質及び触媒担体等から構成されている。図1内に撥水体の濃度分布4を示した。イオン交換膜(電解質)1側での撥水体濃度が高くなるように

調製されている。

【0027】図2の電池は電解質21、電極22、電子伝導体23から構成されている。電極22は触媒成分、撥水体成分、電解質21と同質あるいは異質の電解質及び触媒担体等から構成されている。図2内に撥水体24及び触媒活性成分25の濃度分布を示した。両者とも電解質21側で濃度が高くなるように調製されている。図3の電極は電解質31、電極32、電子伝導体33から構成されている。電極32は触媒活性成分、撥水体成分、電解質31と同質あるいは異質の電解質及び触媒担体等から構成されている。図3内に撥水体34、触媒活性成分35の濃度分布及び気孔率分布36、37を示した。いずれも電解質31側で高くなるように調製してある。気孔率分布36、37についてはどちらかを選択する必要があるが、重要なことは電解質31側で気孔率が低くなるようにしてはならないことである。

【0028】図4の電池は電解質41、電極42、電子伝導体43から構成されている。電極42は触媒活性成分、撥水体成分、電解質41と同質あるいは異質の電解質及び触媒担体等から構成されている。図4内に撥水体44、触媒活性成分45、電解質48、49及び気孔率46、47について分布を示した。電解質48、49は電解質41と同質あるいは異質のものであり48あるいは49の分布から一つを選択する必要がある。重要なことは電極内の電解質成分濃度が電解質41側で低下するような分布を与えてはならないことである。

【0029】図5に濃度分布が不連続である場合の電極構造を示す。電池は電解質51と電極52、53、54及び電子伝導体55からなる。電極は3つの層52、53、54に分割されており、それぞれに含まれる撥水体、触媒活性成分、電解質の濃度分布は図5のように段階的に変化する。また電極内の気孔率も図5のように段階的に変化させることができる。図5では一種類のものの濃度分布しか記載していないが撥水体、触媒活性成分、電解質、及び気孔率のそれぞれを段階的に変化させてもよい。また図5では触媒が三層からなるが特に層の数には限定がない。また以上で述べた電子伝導体とはいわゆる電子伝導性の良い集電体や拡散層等も含む。

【0030】次に図1～図5に示したような濃度分布を有する電極の調製方法を開示する。まず図1～図4のような連続的な濃度分布を形成する方法を開示する。撥水体の分布の調整には塗布法が適している。これは予め電子伝導体上に薄膜として形成した触媒表面に撥水体を分散させた液をブラッシングなどにより塗布したのち、該電極とイオン伝導体を接着するやり方である。例えばカーボンペーパーのような電子伝導体上に塗布した触媒層表面に、PTFEを水に分散した希釈液を塗布することにより図1の4の分布を作製できる。

【0031】イオン伝導体の分布の調整にも塗布法が適している。これは予め電子伝導体上に薄膜として形成し

た触媒表面にイオン伝導体を分散させた液をブラッシングなどにより塗布するやり方である。例えばカーボンペーパーのような電子伝導体上に塗布した触媒層表面に、ナフィオン117などのイオン交換樹脂でイソプロアルコール等に分散された液を塗布することにより図4の48、49の分布を作製できる。

【0032】触媒成分の調整には貴金属を予め担持した触媒層を電子伝導体上に薄膜として形成し、その表面から新たに貴金属成分を付加する方法が良い。その方法としては蒸着、イオン打ち込み等の気相から堆積させる方法などがある。

【0033】気孔率の調整には例えば予め電子伝導体上に薄膜として形成した触媒表面に水蒸気を接触させることにより可能である。水蒸気が触媒層に侵入することにより触媒中に気孔を形成するので水蒸気の流量や濃度キャリアガスの調整により種々の大きさ、分布の気孔の調整が可能である。

【0034】次に図5で示した濃度分布の調整法を開示する。触媒、担体、撥水体、イオン伝導体の濃度を種々調整して図5内触媒層52～54を予め調整しスラリー化する。次に先ず電子伝導体55に触媒層54を塗布する。更に触媒層53、52を順次塗布したのち、イオン伝導体51を接着することにより図5の構造を形成することができる。触媒、撥水体、イオン伝導体の濃度は以上の方法により図5のようなステップ状にすることが可能である。一方、気孔率分布の調整は次ぎのように行う。第一は触媒層52～54をそれぞれ調整する際に含有させる水或いは有機溶媒の量を変化させる方法である。このようにして調整して塗布した触媒層を乾燥すると、水或いは有機溶媒が蒸発する際に気孔を形成し、その大きさや分布は触媒層に添加した水、有機溶媒の量、乾燥速度等により自由にコントロールできる。また第2の方法としては例えば電子伝導体55に塗布した触媒層54の表面に水蒸気を接触させることにより気孔率を変化させることが出来る。乾燥後更に触媒層54上に第2層目の触媒層53を塗布し同様の操作を行う。このよう

な方法によっても触媒層内の気孔率の分布を変化させることが可能である。

【0035】次に上記燃料電池の応用システムを説明する。図10は動力システムを示したものである。水素ガス102、酸素ガス101をレギュレータ103で制御したのち燃料電池104に供給し発電する。燃料電池104からの出力はインバータ105により交流に変換されたのち、モータ等の動力システム106へ供給され、駆動システム107を動作させる。水素ガス102はメタノールなどの改質器により生成されたものを使用することも可能である。

【0036】図11は別の動力システムを示したものである。水素ガス112、酸素ガス111をレギュレータ113で制御したのち燃料電池114に供給し発電する。燃料電池114からの出力はインバータ115により交流に変換されたのち、モータ等の動力システム116へ供給され、駆動システム117を動作させる。水素ガス112はメタノールなどの改質器により生成されたものを使用することも可能である。一方、燃料電池からの出力は二次電池118に充電でき、該二次電池118の出力をインバータ119を介して動力系へ供給することが可能である。

【0037】このシステムでは燃料電池114と二次電池118の内のどちらか一方或いは両方からの出力を動力系に供給することが可能である。

【0038】また図10及び図11のシステムを電気自動車に搭載してもよい。

【0039】(実験例1) 図7に本実験例で使用した電極の構造を示す。図内Bは電解質膜71と水素極74及び酸素極73および拡散層75とからなる。電解質膜としてデュボン社製ナフィオン117を使用した。また拡散層に細孔径約100 $\mu$ m、厚み100 $\mu$ mのカーボンペーパーを使用した。電極73、74の組成を表1に示した。

【0040】

【表1】

表 1

電 極 項 目	7 3	7 2	7 4
P T F E	0.46	0.85	1.5
ナフィオン117	0.51	0.51	1.0
白 金	3.22	3.22	3.0
$\epsilon$	40	40	40

単位  $\text{mg}/\text{cm}^2$  ( $\epsilon$  のみvol%)

【0041】図内Aは電解質膜71と水素極74及び72、73からなる酸素極により構成されている。酸素極72、73及び水素極74の組成を表1に示す。電極Aの特徴は酸素極が二層となっており、電解質膜71側の電極層72中の撥水体であるPTFEの濃度が、外側の電極層73よりも高くなっていることである。

【0042】電極の作製法を以下に示す。先ず前述のカーボンペーパー $150\text{cm}^2$ の上に、表1の組成に従って調製した電極スラリーを均一に塗布した。このあとカーボンペーパーを切りだし $30\text{mm}\times 30\text{mm}$ の電極を作成した。

【0043】図7内Aの酸素電極72、73の作製は次のようにして行った。即ち前述のようにカーボンペーパー上に先ず73の電極を塗布したのち、更に72の電極層を塗布した。

【0044】以上の方法で調製した電極のナフィオンへ\*

20 \*の接着はホットプレス法により行った。AおよびBの構造のものを $100\text{kg}/\text{cm}^2$ の圧力で温度 $120^\circ\text{C}$ で15分プレスした。以上のように作製した電極A、Bをセルに組込み、電流-電圧特性を検討した結果を図8に示した。従来例による電極Bは限界電流密度が $200\text{mA}/\text{cm}^2$ であるのに対して、本発明の電極Aの限界電流密度は $300\text{mA}/\text{cm}^2$ を超えた。このように酸素極を二層化して、電解質膜側の電極の撥水体濃度を高くすることにより、大幅に電池性能を向上することが出来た。

【0045】(実験例2)図9に本実験例で使用した電池を示す。電池はナフィオン膜91、水素電極74、酸素電極92、73及び拡散層93とからなる。電極92、73及び74の組成を表2に示す。

【0046】

【表2】

表 2

電 極 項 目	7 3	9 2	7 4
P T F E	0.46	0.85	1.5
ナフィオン117	0.51	0.51	1.0
白 金	3.22	3.22	3.0
$\epsilon$	40	50	40

単位  $\text{mg}/\text{cm}^2$  ( $\epsilon$  のみvol%)

【0047】この電極の特徴は酸素極が二層化されており、拡散層側の電極73の気孔率は40%であるのに対して、ナフィオン膜側の電極92は気孔率が50%となるように調製してある。

【0048】気孔率の調整は以下のように行った。

50 電極73は50重量%(wt%)白金担持カーボン3.86g、PTFE60%分散液0.27g、ナフィオンのイソプロピルアルコール5%溶液0.31g、純水4ccをらいかい機により混合したのち先のカーボンペーパーに塗布した。これが図9の電極73である。これを80

11

℃で5h乾燥した。次に該電極にさらに50wt%白金担持カーボン3.86g, PTFE60%分散液0.27g, ナフィオンのイソプロピルアルコール5%溶液0.31g, 純水8ccをらいかい機で混合したのち触媒を一層塗布した先の電極に上塗りした。これが図9の電極92である。電極92は調製段階で純水を電極73よりも多量に含有しているので、乾燥時にこの水が蒸発して細孔を形成し、結果的に気孔率が高くなった。

【0049】図8に電極Cの電圧-電流特性を示した。気孔率40%の電極からなる電極Aに対して、酸素極の気孔率を50%と電極Cは限界電流密度が400mA/cm<sup>2</sup>を超え、電池性能が更に向上した。

【0050】

【発明の効果】本発明により高分子電解質を有する酸素-水素型燃料電池の酸素電極の活性を従来のものよりも大幅に向上でき、電池性能を向上できる。

【図面の簡単な説明】

【図1】本発明の電池構造と触媒層内の撥水体の分布を示す説明図。

【図2】本発明の電池構造と触媒層内の撥水体及び触媒活性成分の分布を示す説明図。

\*【図3】本発明の電池構造と触媒層内の撥水体、触媒活性成分、気孔率の分布を示す説明図。

【図4】本発明の電池構造と触媒層内の撥水体、触媒活性成分、イオン伝導体の分布、気孔率の分布を示す説明図。

【図5】本発明の電池構造と触媒層内の撥水体、触媒活性成分、イオン伝導体、気孔率の代表的ステップ分布を示す説明図。

【図6】気孔率の異なる触媒層内の構造を示す概略図。

【図7】(A)及び(B)は電極構造を示す概略図。

【図8】高分子電解質型燃料電池の電圧-電流特性図。

【図9】電極構造を示す概略図。

【図10】本発明の燃料電池を用いた動力システムを示す概略図。

【図11】本発明の燃料電池を用いた他の動力システムを示す概略図。

【符号の説明】

1…イオン伝導体、2…電極、3…電子伝導体、4…撥水体分布、5…界面、101…酸素ガス、102…水素ガス、103…レギュレータ、104…燃料電池、105…インバータ、106…動力システム。

【図1】

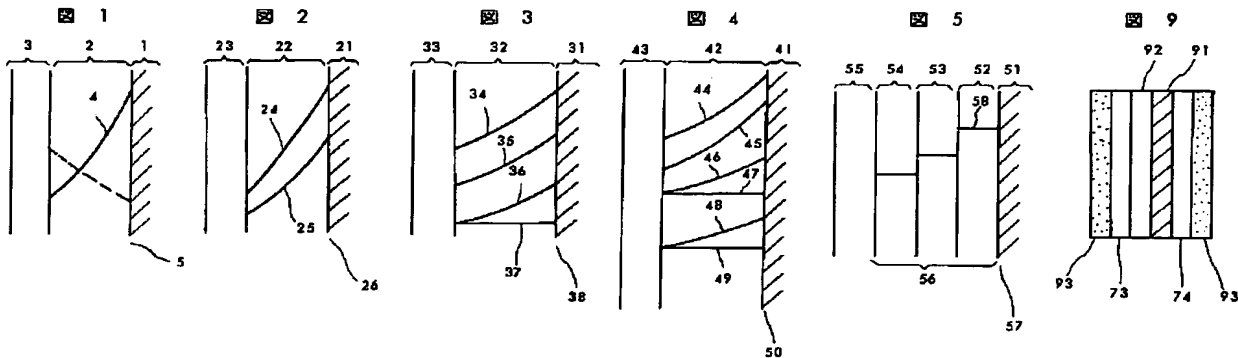
【図2】

【図3】

【図4】

【図5】

【図9】

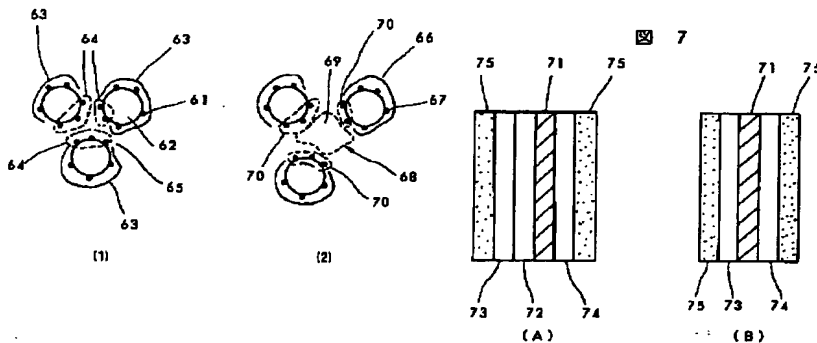


【図6】

図 6

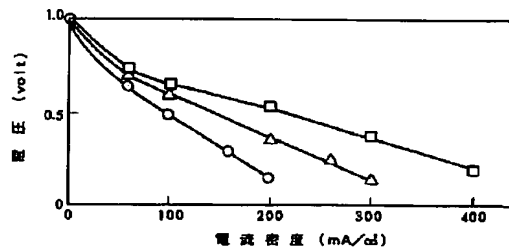
【図7】

図 7



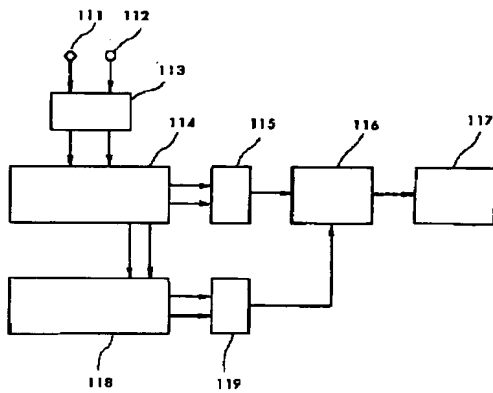
【図8】

図 8



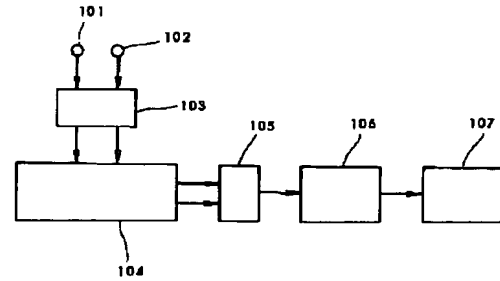
【図11】

図 11



【図10】

図 10



フロントページの続き

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